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Introduction to Polymers, Wood Adhesives, and Wood Finishes

1.1 Good Wood Adhesives Must Be Optimum Polymers with Optimum Secondary Forces

Many structural materials used in this world, including wood adhesives, are hard, strong solid materials, i.e. their softening points (temperatures) are appreciably higher than ambient temperatures. If they become soft or liquid at use temperatures, their structural uses would be limited. Stone, wood, plastics, metals, glass, brick, cotton, etc., are used as structural materials. Liquid adhesives that bond these materials should be transformed into structural solids when the bonding process is completed; otherwise, the bonded elements will separate under a load. Furthermore, among solid materials, certain materials such as sugar or salt have some physical strength under dry conditions, but the strength disappears quickly when they are contacted with water because they dissolve in it, i.e. the molecules become disengaged from each other. Molecular units in structural materials do not disengage from each other easily even when contacted with water or heated to high temperatures since they consist of, firstly, covalently bonded (primary bonding) atoms in the form of high molecular weight polymer molecules (macromolecules), and secondly, these macromolecules also have certain optimum molecular geometry and secondary bonding forces among the atoms and molecules, resulting in solid structures that give strength and stability against exposure to water and/or high temperatures.

For example, the basic chemical structural units in a strand of cotton or wood pulp fibers are cellulose molecules, each having about 5000 or more glucose molecules covalently bonded. It should be reminded that glucose, the basic unit of cellulose polymers, is the main constituent of corn syrup with a molecular weight of 180 and dissolves readily in water due to its low molecular weight and high affinity for water. The major reason why cellulose is cellulose is that the glucose units are bonded together covalently to a high degree of polymerization and also that the secondary forces, exerted by the many hydroxyl groups present on cellulose molecules, are optimally arranged to make the cellulose molecular strands set into crystallites (highly ordered state) that do not get easily disturbed by water. Continuation of these crystallite formation leads to the formation of cellulose fiber strands. Although these fiber strands are further reinforced by lignin and hemicellulose molecules in wood (polymeric glue of wood), much of the strength of wood is derived from the polymeric, structural nature of cellulose molecules and their secondary forces. Thus, it is readily recognized that structural adhesives have to be of (covalently

bonded) polymers that have additional molecular structures and secondary bond forces that impart the strength properties under the common use conditions of moisture and temperature.

1.2 Polymeric Materials

A polymer is defined as a high molecular weight material (macromolecule) composed of many repeating units of a *monomer* or monomers joined by covalent bonds. *Poly* means "many" and "*mer*" means "part," i.e. "polymer" literally means "many joined parts." Polymeric materials can be organic or inorganic and natural or manufactured, as illustrated in the following:

- *Inorganic*: clay, brick, cement, pottery, sand, glass, glass fiber, carbon fiber, metallic carbides.
- *Organic/natural*: polysaccharides (cellulose, starch), proteins (hide, silk), natural rubber from rubber trees (polyisoprene).
- *Organic/synthetic/semi-synthetic*: polyethylene, nylon, polyester, rayon, etc. Monomer materials of synthetic polymers are derived mostly from coal, petroleum, natural gas, and some from wood, like rayon. The diverse properties and many different uses of polymers, as we will see in the next several chapters, can be traced to their high molecular weights and inter- and intramolecular secondary forces (molecular structures) present in the polymer molecules as well as different types (atoms) of monomers. Low molecular weight materials are not useful in most structural applications unless they are transformed into high molecular weight materials during the final forming (curing or molding) steps.

1.3 Synthetic Polymer Preparation Methods

Synthetic polymers are prepared by *polymerization* of monomers [1]. Evidently, the monomers must have two or more hands, i.e. functional groups (that can make covalent bonds), to form a repeating polymer molecular chain. When the monomer (M) has two functional groups, i.e. two free (bonding) electrons, the polymer formed will have a linear chain structure:

$$n \, M = n \, (* \, M \, *) \longrightarrow \quad -M_1-M_2-M_3-M_4-M_5-Mn-$$

<div align="center">Carbon–carbon bond</div>
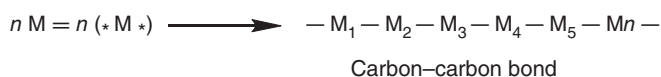
There are currently many different carbon-based monomers having two functional groups. When monomers having three or more functional groups are used, the polymer chain will be branched and, at the end of polymerization, the polymer molecules will be cross-linked. Also, aside from the common C—C bonds, the C—O bonds (ethers and esters), and C—N bonds (amides) are common chemical bonds formed in polymers. The end groups in polymers are not normally defined clearly in equations, but they are only slightly different groups than those in the middle of the chain, formed by some

side reactions at the end of the polymerization process. The end groups are of minor importance in polymer technology because the value "*n*," *degree of polymerization*, reaches one thousand or more, and, therefore, the proportion of end groups in the entire polymer molecule becomes exceedingly small.

1.4 Typical Synthetic Polymer Materials

- *Polyethylene*: One ethylene molecule (gas) is added to another ethylene molecule, another ethylene molecule, etc., often called an "addition polymerization," with the help of a catalyst and under pressure. Ethylene itself is a gas at ordinary temperatures, and polyethylene is a thermoplastic solid material; the difference being the high molecular weight of the latter, attained by polymerization. Uses and properties: bottles, containers, films for packaging (shopping bags), and high-strength fiber. Polyethylene softens when heated to 95–120 °C and finally melts at higher temperatures (a thermoplastic polymer); at room temperature, it is stretchable, flexible, hydrophobic, etc. It has been the largest volume polymer among all synthetic organic polymer materials.

$$n \ CH_2{=}CH_2 \longrightarrow [* \ CH_2{-}CH_2 \ *] \longrightarrow -(CH_2{-}CH_2)_n-$$
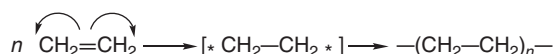
- *Polypropylene*: A thermoplastic addition polymer made by (head to tail) polymerization of propylene as monomer. Uses and properties: laboratory beakers, bottles, ice chests, rope, etc.; it softens when heated to about 150 °C (thermoplastic), similar to polyethylene, but is stiffer and the softening point is higher.

$$n \ CH_2{=}CH \longrightarrow -(CH_2{-}CH)_n- \\ \qquad\ \ | \qquad\qquad\qquad | \\ \qquad\ \ CH_3 \qquad\qquad\quad CH_3$$
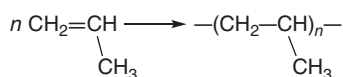
- *Polystyrene*: A thermoplastic addition polymer made by (head to tail) polymerization of styrene as monomer. Commercial polystyrene polymers normally have an average molecular weight in the range of 50–200 k Da and are extensively used as expanded materials, such as cups and dishes, and for insulation and package sheeting.

$$n \ CH_2{=}CH \longrightarrow -(CH_2{-}CH)_n-$$
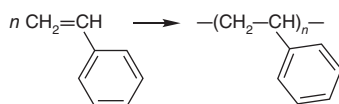
- *Polyvinyl acetate (PVAc)*: A thermoplastic addition polymer made by (head to tail) polymerization of vinyl acetate as monomer, commonly done as an emulsion polymerization process to result in latices. The glass transition (softening) temperature of commercial solid PVAc polymers is about 28 °C, and they are modified with 10–15% plasticizer (dibutyl phthalate) for use as wood binders and in coatings. Uses and properties: wood glue, interior use paint vehicle (binder). It melts when heated (thermoplastic) and has the polar characteristics needed for wood adhesive polymers due to the presence of polar acetate (—O—Ac) groups in comparison to polyethylene or polypropylene.

$$n\ CH_2{=}CH \longrightarrow -(CH_2{-}CH)_{n'}-$$

with pendant $O{-}C{=}O{-}CH_3$ (acetate) groups on each unit.
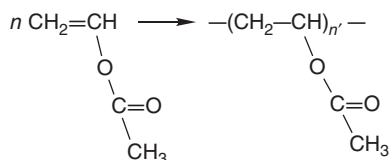
- *Ethylene-vinyl acetate (EVA) co-polymer*: A thermoplastic "co-polymer" made by co-polymerizing ethylene (5–20% by weight) and vinyl acetate monomers. The resultant co-polymer materials show high clarity, low-temperature flexibility, and crack resistance. The polymers are more flexible than PVAc. The co-polymers made with about 20% ethylene contents are used as hot-melt adhesives used in wood and paper bonding.

$$n\ CH_2{=}CH_2\ +\ n'\ CH_2{=}CH \longrightarrow -(CH_2{-}CH_2)_n{-}(CH_2{-}CH)_{n'}-$$
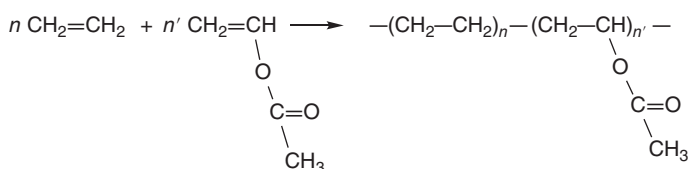
- *Polyvinyl chloride*: A thermoplastic polymer made by polymerizing (head to tail) vinyl chloride as a rigid, colorless polymer. With the addition of stabilizers and fillers, they are used extensively as water pipes, coatings, etc.

$$-(CH_2{-}CH)_n-$$
with pendant Cl
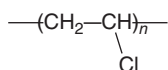
- *Acrylics*: Acrylic acid (i) and methacrylic acid (iv), their ester and amide derivatives (ii, iii, and v), and cyanoacrylic acid esters (vi) are the monomers for acrylic resins. Monomers are polymerized, respectively, through their double bonds to result in high molecular weight thermoplastic emulsion (latex) polymer materials, which are widely used as coatings, adhesives, and pane glasses.

$$CH_2{=}CH{-}COO{-}X \longrightarrow \left[CH_2{-}CH(COO{-}X)\right]_n$$
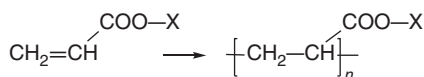
(i) Acrylic acid (X=H): **(ii)** Acrylic esters (X=methyl or ethyl groups): **(iii)** Acrylamide (X=NH$_2$ group).

$$CH_2{=}C(CH_3){-}COO{-}X \longrightarrow \left[CH_2{-}C(CH_3)(COO{-}X)\right]_n$$
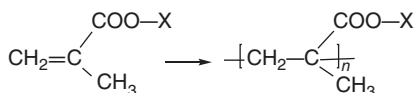
(iv) Methacrylic acid (X=H): **(v)** Methacrylic esters (X=methyl or ethyl groups)

$$CH_2{=}C(C{\equiv}N){-}COO{-}X \longrightarrow \left[CH_2{-}C(C{\equiv}N)(COO{-}X)\right]_n$$
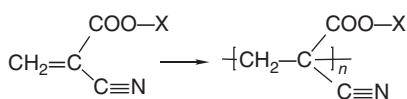
(vi) Cyanoacrylic esters (X=methyl or ethyl groups)

- *Nylon*: A polyamide, thermoplastic, made by condensation polymerization of a dicar-boxylic acid and a diamine as monomers: the two monomers are condensed in exactly $1.00 : 1.00$ mol ratio, where a water molecule is expelled to form amide bonds (conden-sation polymerization reaction). Uses and properties: filament yarn (nylon, clothes) and engineering composites and moldings. They melt when heated and are flexible, stretch-able, and strong.

$$n\ HO_2C—(CH_2)_4—CO_2H \quad + n\ H_2N—(CH_2)_6—NH_2 \xrightarrow[-nH_2O]{Condensation}$$

$$n\ HO_2C—(CH_2)_4—\mathbf{CO}\big[—\mathbf{HN}—(CH_2)_6—\mathbf{NH}—\mathbf{OC}—(CH_2)_4—\mathbf{CO}\big]_n—\mathbf{HN}—(CH_2)_6—NH_2$$

Amide bond
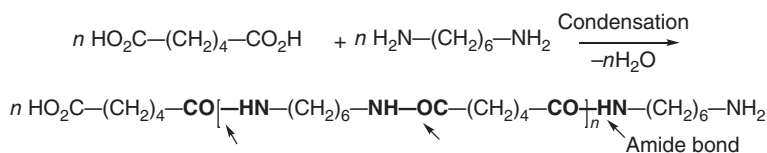
- *Polyesters*: A thermoplastic polymer made by condensation of a diol and a dicarboxylic acid as monomers. Uses and properties: filament yarn (polyesters, clothes, and polyester fibers, bottles, etc.) They melt when heated and are less hydrophobic than polyethylene or nylon. There are a variety of diols and diacids used to make polyesters and one class of them is alkyd resins used extensively as coating vehicles for wood.


Ester bond
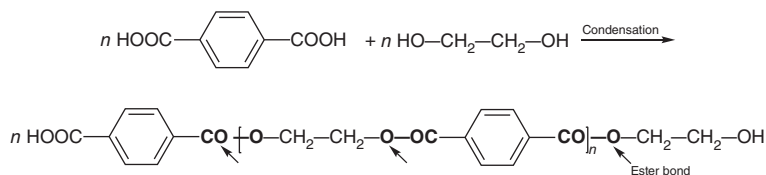
- *Phenol-formaldehyde (PF) resins*: Condensation polymers of formaldehyde and phenol as monomers; phenol has three functional groups and formaldehyde has two, use of less than 1.0 mol of formaldehyde leads to the novolac-type resins as shown, which need more formaldehyde in the curing step (two-step PF resins), and use of more than 1.0 mol of formaldehyde in resin synthesis leads to resole-type resins that cure directly (one-step PF resins). Uses and properties: wood adhesives for softwood plywood and oriented strand board, molding compounds for pot handles, etc.


Novolac-type RF resin
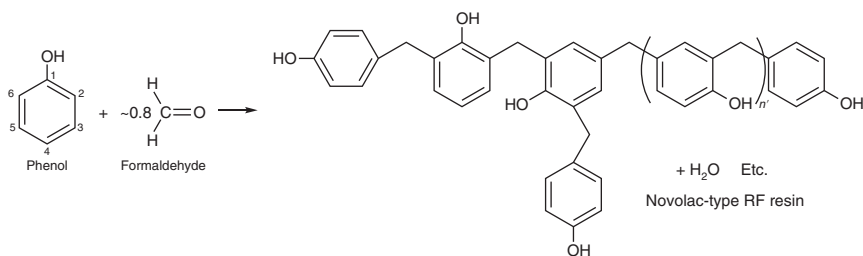
PF resins, once polymerized to final articles or gluelines, do not melt because of the branched (three dimensional) and cross-linked structures of polymer chains. In order to make an article using PF novolac resins, a source of formaldehyde is added, and it is

then put in a mold, and heat and pressure are applied until the polymerization reaction is complete. PF resole-type resins do not need the second formaldehyde.

- *Resorcinol-formaldehyde resins*: Condensation polymers of resorcinol and formaldehyde are synthesized with about 1.0 : 0.7 mol ratios, novolac-type resins, as shown. Addition of some more formaldehyde and curing leads to cured RF resin polymers. They are thermosets similar to novolac PF resins in formalism, but their reactivity is greater, and they are used as room temperature-curing wood adhesives and other applications such as tire cord-rubber binders.
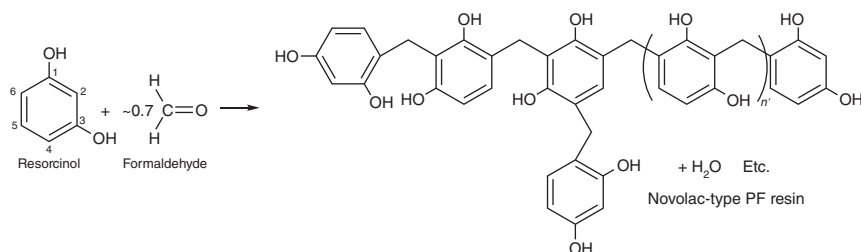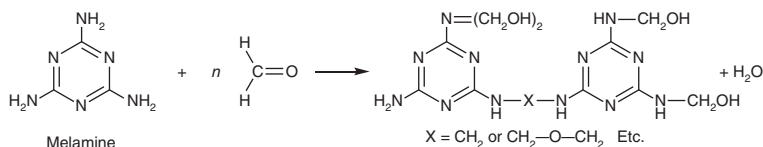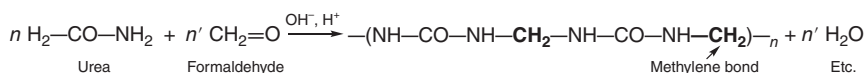

- *Isocyanate resins*: Isocyanate resin monomers are manufactured in industry to have two or more isocyanate groups (—N=C=O) per monomer molecule, and several aromatic (AR) and aliphatic (R) group-based commercial isocyanate resins are available. Isocyanate monomers are then reacted with diols (HO—R—OH) or diamines (NH_2—Ar′—NH_2) of various kinds to form *urea (AR—**NH—CO—NH**—Ar′′—**NH—CO—NH**—AR—) or urethane (AR—**NH—CO—O**—R—**O—CO—NH**—AR) bonds* to result in high molecular weight *thermosetting* materials. Aromatic group-based isocyanate resin materials such as diphenylmethane 4,4′ and 2,4′ di-isocyantes (dimers) are used in large volumes in foam manufacture, and the higher oligomeric (trimer ~ hexamer) isocyanate materials (pMDI) are much used as core-layer binders of oriented strand boards and in preparation of various coating vehicles.

Reaction of isocyanate groups with amine groups in polymer formation
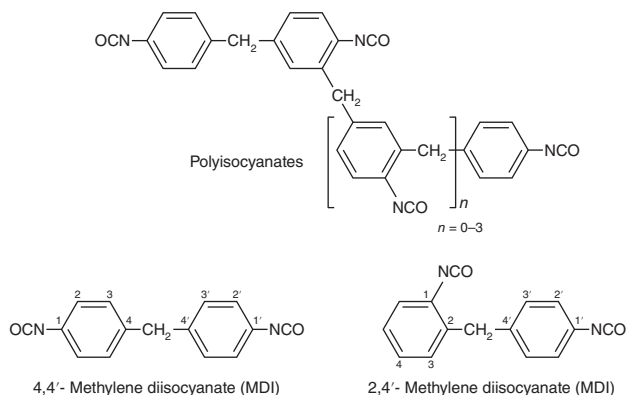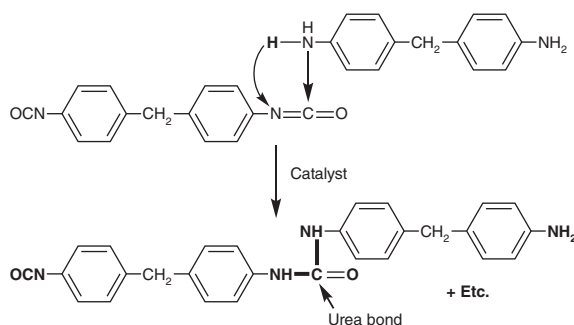
- *Urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins*: Urea or melamine is reacted with formaldehyde in 1.0 : 1.1–1.8 mol ratios to make thermosetting resin materials and then cured by catalysts and heating to cross-linked polymers as adhesive binders for wood composite boards and wood moldings. They are used in the manufacturing of interior-grade particleboard, fiberboard, and laminated beams and are also used as cross-linkers in some thermosetting coatings.

$$n\ H_2-CO-NH_2\ +\ n'\ CH_2=O\ \xrightarrow{\ OH^-,\ H^+\ }\ -(NH-CO-NH-CH_2-NH-CO-NH-CH_2)-_n\ +\ n'\ H_2O$$

Urea   Formaldehyde   Methylene bond   Etc.

Melamine   X = CH_2 or CH_2-O-CH_2 Etc.

- *Epoxy resins*: Epoxy resins have two or more epoxy groups in a monomer molecule that react with primary and secondary amino groups of hardener parts as well as with hydroxyl groups generated in the process to result in thermosetting cross-linked polymers. They are used extensively as matrix resins in engineering composite materials and as specialty adhesives.
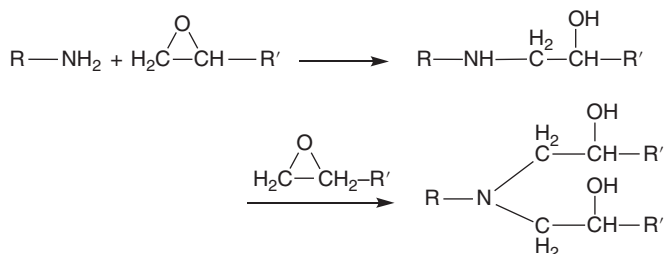
1.5   Typical Natural Polymers

- *Cellulose*: In cellulose, glucose molecules are the monomers, polymerized via 1,4′-linkages in the beta conformation by forming acetal bonds on the aldehyde groups (Carbon No. 1) as shown. The degree of polymerization, n, reaches several thousand or more, depending on the origin of cellulose: cotton, linen, wood pulp, rayon, ramie, etc., and even different woods have celluloses that are different in the degree of polymerization. Celluloses are linear polymers, but when they are heated to a high temperature, they decompose before they reach the melting point. The cellulose chains in wood exist in crystallites (highly ordered state) in which the many hydroxyl groups exist in tightly hydrogen-bonded structures (secondary bonding forces), and some portions are also in amorphous forms. Various derivatized cellulose polymers are currently manufactured by reacting various mono-functional chemicals on the cellulose hydroxyl groups to form ester or ether groups, as shown in the following examples:
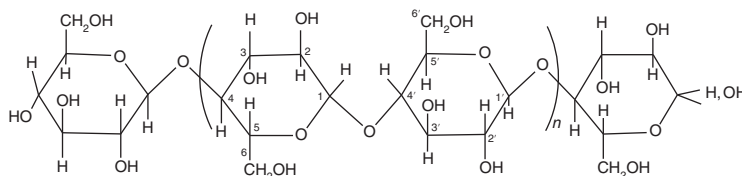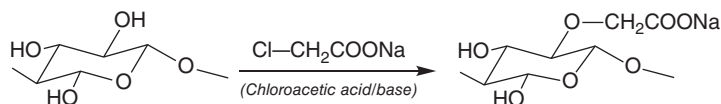

- *Cellulose nitrate (ester)*: It is made by reacting cellulose with a nitric acid/sulfuric acid mixture, and the resultant cellulose nitrate polymers are used to make various "celluloid" products, such as films for recording movies, lacquer (coating) polymers for wood finishes, and gun powder (highly nitrated materials).
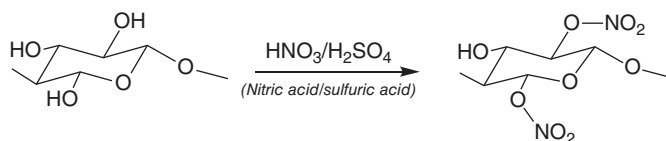

- *Cellulose acetate (ester)*: It is made by reacting with acetic anhydride, and it is used as acetate rayon yarn, i.e. silk substitute clothes, and lacquers.
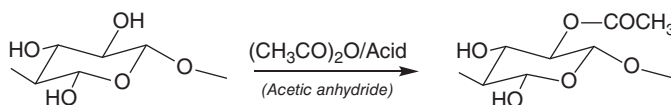

- *Carboxymethyl cellulose (ether)*: It is made by reacting with sodium chloroacetate, and it is used as food additives, wallpaper adhesives, etc.
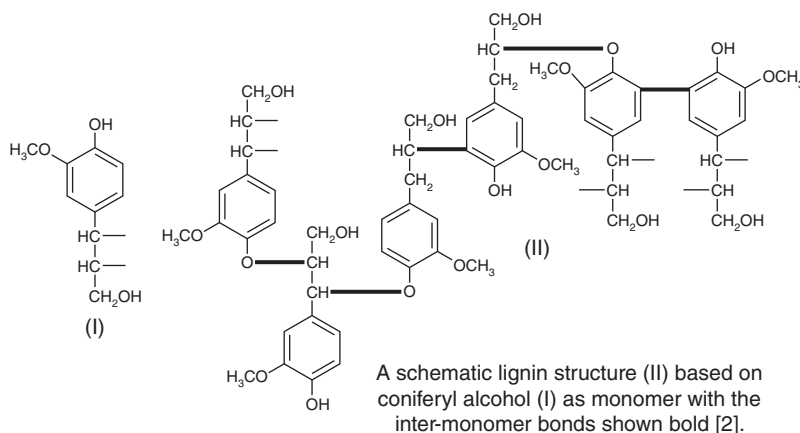
- *Hydroxyethyl cellulose (ether)*: It is made by reacting with ethylene oxide, and it is used as thickeners in paints and adhesives, etc.
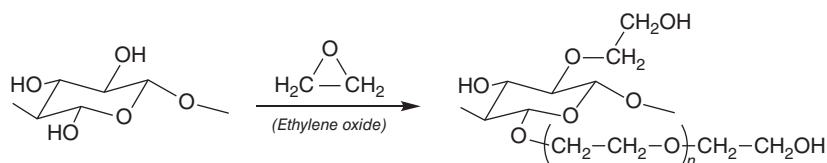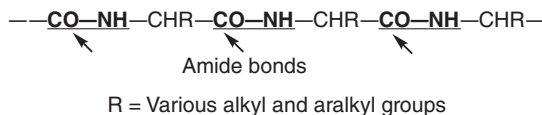

- *Starch*: It occurs in nature, in which glucose molecules are polymerized into 1,4′- and 1,6′-linkages with alpha configuration different from that of celluloses. They are obtained from plants as mixtures of (linear) amylose and (branched) amylopectin. The degree of polymerization is high and variable depending on the origin: potato, corn, wheat, tapioca, etc., and they swell in water when cooked. Used in food, interior use adhesives for corrugated paper products, and others.

Amylopectin   Amylose
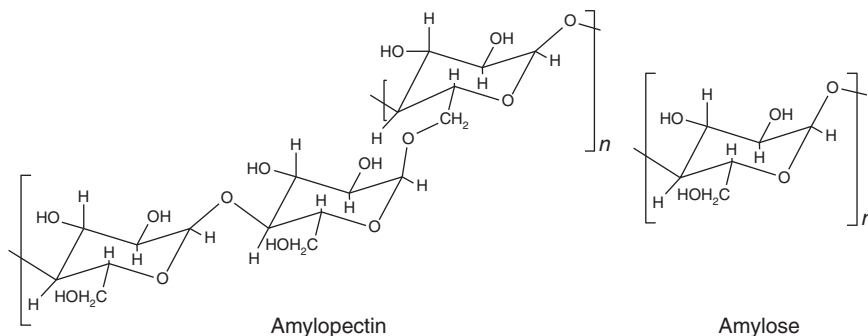
- *Lignin*: "Lignin" components, together with hemicellulose components, are the adhesive polymers of cellulose fibers in wood. Wood pulps manufactured in the wood pulping industry are primarily composed of undigested cellulose molecules, and the lignin polymers and hemicellulose molecules are dissolved and partially decomposed to come out as black liquor in the Kraft pulping process. Black liquors are used as an energy source for the pulping plant. In lignin molecules, phenolic rings are present in polymerized forms, in a somewhat irregular, branched manner, connected through the 3-carbon aliphatic side chains, forming "ether" bonds with phenolic oxygens of another ring. Intact natural lignin polymers are difficult to isolate, and therefore the accurate structures of lignins have been difficult to determine, and they vary depending on the origin of wood. "Industrial lignin" products from the sulfite pulping processes are lignosulfonates, available for use as additives in wood adhesives and in other applications.

A schematic lignin structure (II) based on coniferyl alcohol (I) as monomer with the inter-monomer bonds shown bold [2].

- *Proteins*: Most proteins are natural *polyamide polymers* of various "alpha-amino acids," as shown below. The functional groups involved in polymerization are the amine and carboxylic acid groups, as in nylon-type polyamide polymers. Twenty or so different amino acids occur in nature (with various R groups), and many combinations are possible depending on the origins of protein materials, but industrial proteins useful as adhesives are casein from milk, animal tissue proteins (collagen), blood proteins (albumin), and soybean proteins.

$$-\!-\textbf{CO}\!-\!\textbf{NH}\!-\!CHR\!-\!\textbf{CO}\!-\!\textbf{NH}\!-\!CHR\!-\!\textbf{CO}\!-\!\textbf{NH}\!-\!CHR\!-$$

Amide bonds

R = Various alkyl and aralkyl groups

1.6 Summary

Wood adhesive gluelines are solid structural materials consisting of many molecules of organic polymers and fillers, molecularly structured in ways to withstand the external loads and environmental influences. Organic polymer molecules are made in laboratory or by nature, where monomers are first created and then polymerized to very high molecular weight polymers. Monomers are commonly gases, liquids, or solids with molecular weights lower than about 200 Da, and polymers are mostly solids having high molecular weights of up to 100 000 Da or higher, or unmeasurable. Various monomers and mechanisms of polymerization are presented. Many monomers are relatively simple molecules that have a carbon–carbon double bond (C=C), one of which is opened by catalysts to form carbon–carbon (C—C) covalent bonds with other monomers almost endlessly (addition polymerization) reaching to high molecular weight materials. Thus, ethylene gas is polymerized to polyethylene, propylene to polypropylene, styrene to polystyrene, etc. On the other hand, condensation polymers are formed between two different monomers such as —N=C=O groups of the first monomer reacting with a hydroxyl or an amino group of the second monomer to form polyurethane and polyurea polymers, respectively. Similarly, dicarboxylic acid groups of the first monomer condensed at exactly 1.00 : 1.00

group ratios with dihydroxyl or diamine groups of another monomer to form condensation polymers such as polyesters or polyamides with the expulsion of water molecules. Proteins are a special case of condensation polymers where many different amino acids, each having a carboxylic acid and an amino group, co-polymerize to form polyamides, i.e. protein polymers. Similarly, monomers having an aldehyde group and hydroxyl groups, such as glucose monomer, open the aldehyde C=O double bond and condense with two hydroxyl groups to form acetal bonds, resulting in poly-glucoses, such as cellulose and starch. Cellulose and starch can be derivatized on their hydroxyl groups by ether or ester bond formation to nitrocellulose and other derivative polymers. Monomers having two or more epoxy groups polymerize by opening the triangular epoxy bonds to form polyether polymers or polymerize with diamines to form thermosetting cross-linked epoxy polymers. Further, a monomer is formed by reacting two different components, such as formaldehyde with phenol, resorcinol, urea, or melamine, to form hydroxymethyl derivatives, which are then activated by an acid or base catalyst to polymerize into high molecular weight cross-linked polymers. These latter-group polymers are the major polymer materials used as thermosetting adhesives in bonding of wood and wood composite boards.

References

1 Saunders, K.J. (1988). *Organic Polymer Chemistry*, 2e. London and New York: Chapman and Hall.
2 Sarkanen, K.V. and Ludwig, C.H. (1988). *Lignins, Occurrence, Formation, and Structure and Reactions*. New York: Wiley.